Superconductivity of filled skutterudites $LaRu_4As_{12}$ and $PrRu_4As_{12}$

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Ternary ruthenium arsenides with the skutterudite structure, $LaRu_4As_{12}$ and $PrRu_4As_{12}$ have been prepared at high temperatures and high pressures. Electrical and magnetic properties of both compounds have been studied at low temperatures. Superconductivity in $LaRu_4As_{12}$ and $PrRu_4As_{12}$ was found at around 10.3 and 2.4 K, respectively. The T_c of $LaRu_4As_{12}$ is the highest amongst skutterudite compounds. The specific heat of $LaRu_4As_{12}$ has been measured between 2 and 20 K. The specific-heat data can be fit to the expression $C = \gamma T + \beta T^3$, where $\gamma = 73$ mJ/mol K^2 and $\beta = 2.6$ mJ/mol K^4, resulting in a Debye temperature (Θ) of 233 K. $PrRu_4As_{12}$ is the only known superconductor within the family of magnetic rare-earth filled skutterudites. The arsenic plays an important role for the enhancement of superconductivity in both arsenides. Properties of the superconductivity of $LaRu_4As_{12}$ and $PrRu_4As_{12}$ are discussed. [S0163-1829(97)03637-0]

INTRODUCTION

Ternary metal pnictides with the general formula LT_4X_{12} (L = lanthanide; T = Fe, Ru, and Os; X = pnicogen) crystallize in a skutterudite ($CoAs_3$-type) structure filled by lanthanide atoms.[1,2] L atoms locate at (000) and (1/2 1/2 1/2) of a cubic structure like bcc. The transition-metal atoms (T) are in the center of a distorted octahedral environment of six pnicogen atoms. The skutterudite structure is characterized by the formation of well-defined X_4^{4-} groups. These filled skutterudites show interesting electrical and magnetic properties at low temperatures. One of the most striking features of these compounds is the occurrence of superconductivity in $LaFe_4P_{12}$ with a superconducting transition temperature (T_c) of 4.1 K.[3,4] $LaRu_4P_{12}$ and $LaOs_4P_{12}$ with the skutterudite structure are also superconductors with T_c = 7.2 and 1.8 K, respectively.[3–5]

We have prepared many filled skutterudites LRu_4X_{12} (L = La, Ce, Pr, Nd, Sm, Gd, and Tb; X = pnicogen) at high temperatures and high pressures.[6] Electrical and magnetic properties of these compounds have been studied at low temperatures. Superconductivity in filled skutterudites has been observed for $LaRu_4As_{12}$ and $PrRu_4As_{12}$ with T_c's of 10.3 and 2.4 K, respectively. $LaRu_4As_{12}$ has the highest T_c in the skutterudite compounds. $PrRu_4As_{12}$ is the only known superconducting magnetic rare-earth filled skutterudite. In this paper the superconducting properties of $LaRu_4As_{12}$ and $PrRu_4P_{12}$ are discussed.

EXPERIMENT

Using a wedge-type cubic-anvil high-pressure apparatus, LRu_4X_{12} (L = La and Pr; X = P, As, and Sb) were prepared at high temperatures and high pressures.[6] The upper and lower

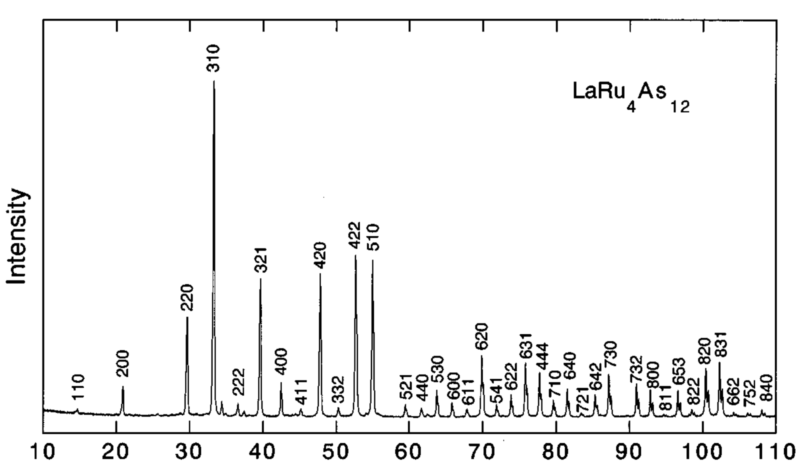

FIG. 1. X-ray-diffraction pattern of $LaRu_4As_{12}$ prepared at high pressure.

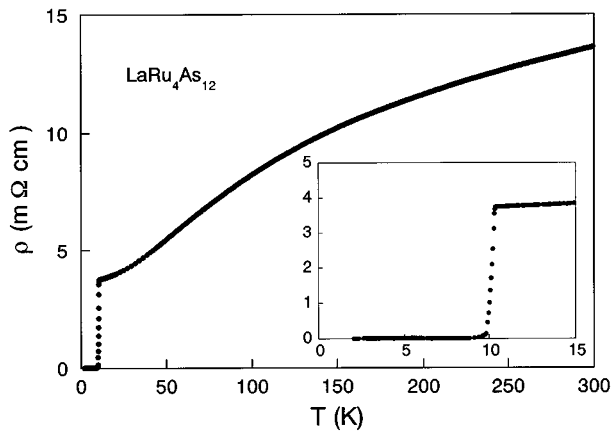

FIG. 2. Temperature-dependent resistivity between 300 and 2 K for $LaRu_4As_{12}$.

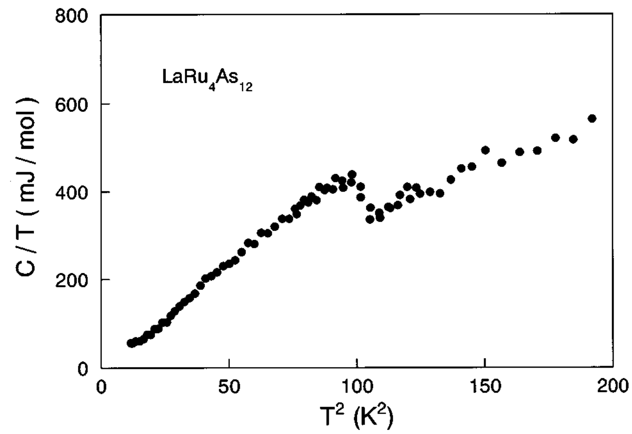

FIG. 4. Low-temperature specific heat of $LaRu_4As_{12}$.

stages of the high-pressure apparatus consist of three anvils that slide on the wedge formed in shallow V-shaved grooves. The anvil movement is completely synchronized by means of a wedge system. The anvils prepared from cemented tungsten carbide have a 16×16 mm^2 top-square face. The sample container made of pyrophyllite is formed into a cube of 21 mm on an edge. The sample assembly for the preparation of the filled skutterudites is similar to that used for the synthesis of black phosphorus.[7] The starting materials are put into a crucible made of BN. The crucible with a graphite heater is inserted into the pyrophyllite cube.

The ternary ruthenium arsenides were prepared by reaction of stoichiometric amounts of each metal and arsenic powders at around 4 GPa. The reaction temperatures were between 800 and 900 °C for $LaRu_4As_{12}$ and $PrRu_4As_{12}$. The samples were characterized by powder x-ray diffraction using Cu $K\alpha$ radiation and silicon as a standard. Figure 1 shows the x-ray-diffraction pattern of $LaRu_4As_{12}$. A similar pattern was also observed for $PrRu_4As_{12}$. All diffraction lines of both arsenides prepared at high pressure are assigned by the index of the skutterudite structure. The lattice constants of the arsenides agree with the results obtained by Braun and Jeitschko.[2] The ratio of composition of the compounds prepared at high pressure is confirmed by electron probe microanalyzer (EPMA).

Copper or gold lead was attached to polycrystals of the samples with silver filled by epoxy, and four-lead electrical resistivity measurements were performed at low temperatures. The dc magnetic susceptibility of the polycrystalline samples was measured in the range of 1.8–300 K with a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The adiabatic specific-heat measurement for $LaRu_4As_{12}$ was performed in the temperature range between 2 and 20 K.

RESULTS AND DISCUSSION

Figure 2 shows the resistivity of $LaRu_4As_{12}$ at low temperatures. The resistivity decreases with decreasing temperature and sharply drops at around 10.3 K. Figure 3 shows the temperature dependence of the dc susceptibility measured in an applied magnetic field of 5 Oe for $LaRu_4As_{12}$. The susceptibility of the arsenide sharply decreases at around 10.3 K. The sample cooled in zero field shows a magnetic shielding equal to approximately 100% of that expected for perfect diamagnetism. The existence of hysteresis between zero-field cooling (ZFC) and field cooling (FC) indicates that the arsenide is a type-II superconductor. Figure 4 shows the result of the specific-heat measurement of $LaRu_4As_{12}$ at low tem-

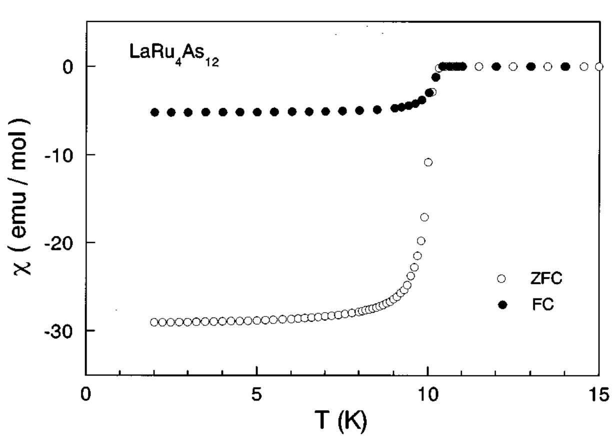

FIG. 3. dc susceptibility vs temperature curve (applied field $B=5$ Oe) for $LaRu_4As_{12}$.

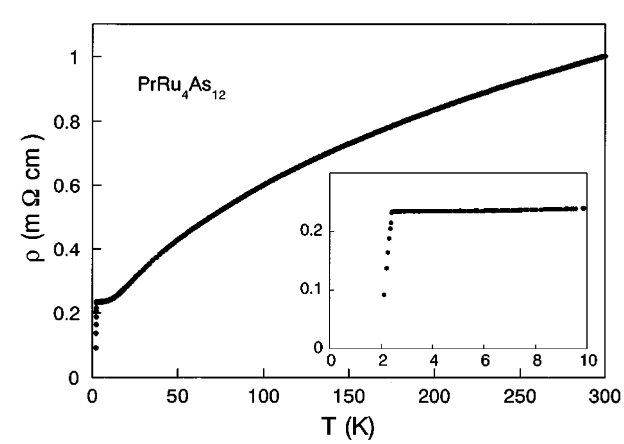

FIG. 5. Temperature-dependent resistivity between 300 and 2 K for $PrRu_4As_{12}$.

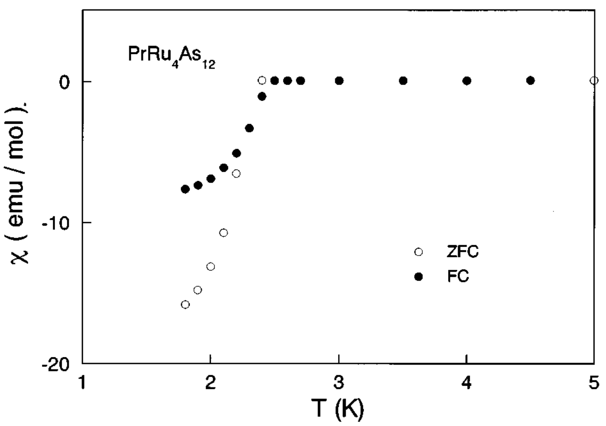

FIG. 6. dc susceptibility measured in the field of 5 Oe for $PrRu_4As_{12}$ at low temperatures.

peratures. The heat capacity C of the compound can be fit to the expression $C=\gamma T+\beta T^3$ by a least-squares analysis, which yields the value $\gamma=73$ mJ/mol K^2 and $\beta=2.6$ mJ/mol K^4, the latter value corresponding to the Debye temperature $\Theta=233$ K. Since the specific-heat jump ΔC is 1290 mJ/mol K at T_c (=10.1 K), $\Delta C/\gamma T_c$ is 1.75. This value is slightly larger than 1.43 of BCS theory.

Further, we have investigated the electrical and magnetic properties of $LaRu_4Sb_{12}$ at low temperatures and found the superconducting transition at around 2.8 K for $LaRu_4Sb_{12}$.

Figure 5 shows the resistivity vs temperature curve for $PrRu_4As_{12}$. The resistivity decreases with decreasing temperature and sharply drops at around 2.4 K. Figure 6 shows the susceptibility measured in a field of 5 Oe at low temperatures. A large diamagnetic susceptibility is found at around 2.4 K.

T_c's of the superconducting skutterudites compounds are summarized in Table I. The T_c of $LaRu_4As_{12}$ is the highest in these compounds. $PrRu_4As_{12}$ is the only known superconductor with a magnetic rare earth in the skutterudites compounds. There are a few superconductors containing arsenic. ZrRuAs with Fe_2P-type structure has a T_c of 11 K,[8,9] but is lower than the T_c (=13 K) of ZrRuP.[10,11] The black-phosphorus–arsenic alloys have the T_c's of 6–10 K at very high pressures.[12,13] However, the T_c of the alloys decreases with increasing concentration of arsenic. The T_c of the superconductivity of both materials is not enhanced by arsenic. On the contrary, the T_c of $LaRu_4As_{12}$ is 3 K higher than that of $LaRu_4P_{12}$. The compound $PrRu_4As_{12}$ is of special interest since superconductivity in $PrFe_4P_{12}$,[3] $PrRu_4P_{12}$, and $PrOs_4P_{12}$ (Ref. 14) is not observed down to 2 K. The band electronic structure of $LaFe_4P_{12}$ has been calculated by employing the tight-binding method within the extended Hückel framework; the major contribution to the highest occupied band of the phosphide comes from the orbitals of the P_4 rings that form the phosphorus sublattice.[15] The compound CoP_3 with skutterudite structure is a semiconductor, but $CoAs_3$ seems to be metallic.[16] A recent band structure calculation suggests that $CoAs_3$ is actually a zero- and narrow-gap semiconductor.[17] If phosphorus atoms in the skutterudite compounds are substituted by arsenic atoms, the electronic states of the metal arsenides must change significantly in the vicinity of Fermi level. The enhanced superconductivity of $LaRu_4As_{12}$ and $PrRu_4As_{12}$ may mainly arise from the change of the electronic states.

TABLE I. T_c's and lattice constants of superconducting filled skutterudites.

Compounds	a(Å)	T_c (K)
$LaFe_4P_{12}$	7.8316	4.1
$LaRu_4P_{12}$	8.0561	7.2
$LaOs_4P_{12}$	8.0844	1.8
$LaRu_4As_{12}$	8.5081	10.3
$PrRu_4As_{12}$	8.4963	2.4
$LaRu_4Sb_{12}$	9.2700	2.8

The superconductivity of the ternary chalcogenides LMo_6S_8 persists across the entire rare-earth series, with exception the Ce and Eu members.[18] The T_c of $PrMo_6S_8$ is 2.55 K. Fischer *et al.* suggest the exchange interaction between the superconductivity electrons and rare-earth ions, and the interaction between rare-earth ions are weak.[18] On the other hand, the physical properties of $PrBa_2Cu_3O_7$ have been studied extensively in order to understand the absence of superconductivity in this compound.[19] $PrBa_2Cu_3O_7$ reveals antiferromagnetic ordering of the Pr ion at low temperatures.[20]

The electrical and magnetic data in the compounds LT_4P_{12} show not only the absence of superconductivity for the magnetic rare earths, but the magnetic ordering indicates a strong magnetic interaction between the rare-earth ions.[3] We have found a metal-to-insulator transition at around 60 K for $PrRu_4P_{12}$; the resistivity of the phosphide decreases with decreasing temperature from 300 to 60 K, and abruptly increases with decreasing temperature below 60 K.[14] Meisner has reported that the ac susceptibility of $PrRu_4P_{12}$ shows an upturn that is still increasing at 0.35 K, indicating possible ordering at lower temperatures.[3] However, $PrRu_4As_{12}$ shows a superconducting transition at around 2.4 K. This is the only known magnetic rare-earth skutterudite compound which superconducts.

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